

Diethyl Ether Production Process with Various Catalyst Type

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Abstract - Several H-zeolite and HZSM-5 catalysts was prepared and their characters have also been investigated. H-zeolit Catalyst was prepared from Natural Zeolite that obtained from Malang District and Gunung Kidul District. Diethyl ether was produced by Ethanol with concentration of 95%. This research use fixed bed reactor that 1 gram of catalyst as bed catalyst, atmospheric pressure and temperature 140°C as the operating condition. Ethanol vapor from vaporization tank was driven by 200 ml/min Nitrogen stream. The responds in this research is liquid product concentration; diethyl ether, ethanol, methanol and water concentration. The results showed that the largest ethanol conversion was produced by the use of 56.44% HZSM-5 and the largest yield of diethyl ether diethyl was produced by the use of alumina and H-zeolite catalyst. The larger ratio between natural zeolite with HCl solvent will produce the larger surface area of catalyst and ethanol conversion. The largest ethanol conversion was produced at reactan ratio 1:20.

[Keywords: catalyst; ethanol conversion; dehydration process; yield of diethyl ether; natural zeolite].

I. INTRODUCTION

Diethyl ether is one of the most important commercial ether. In industry, Diethyl ether is often used as a solvent of organic reactions such as oil, fat, latex, micro cellulose, perfume, alkaloid solvent. This ether is also used as a separator of organic compound from its natural material sources. In addition, diethyl ether is identical to anesthesia in medical science^[1].

Diethyl ether can be produced using homogenous catalyst (sulfuric acid/Barbet process) and heterogeneous catalyst. The difficulty of Catalyst separation becomes the weakness of Barbet process. Furthermore, the corrosive behavior of Barbet process causes this process becomes costly. The second process, heterogeneous catalyst, uses alumina catalyst. In this process, ethanol conversion per pass and its yield is 60-80 and 90% respectively^[1]. Butt, et al^[2] and de Boer, et al^[3], studied kinetic reaction of this process.

Evidently, the use of alumina catalyst in ethanol dehydration process produces a low ethanol conversion and diethyl ether yield. Therefore, researchers develop the type of catalyst that can be used for ethanol hydration and dehydration process such as Alumina, MgO, alumina silica and WO₃ catalyst^[4]. In addition, zeolite can also be used for this process. Takahara, et al^[5] used H-modernite type of zeolite for ethylene production. In this production process, ethanol was dehydrated to be diethyl ether and subsequently becomes

ethylene. The result showed that H-modernite with ratio of SiO₂/Al₂O₃ 90 is more stable than H-modernite with SiO₂/Al₂O₃ 20^[5]. Haber, et al^[6] has a research about ethanol dehydration process with Kalium saline and silver from tungstophosphoric acid (HPW) by varying the type and the number of cation K_xH_{3-x}PW₁₂O₄₀ and Ag_xH_{3-x}PW₁₂O₄₀. In his research, value of x was varied in the range of 0<x<2 for K_xH_{3-x}PW₁₂O₄₀ and 0<x<3 for Ag_xH_{3-x}PW₁₂O₄₀. The result showed that the catalytic activity of the both process was improved. This result shows that catalytic activity has a relation to proton acid and proton that is produced by silver cation. In a high temperature (T > 573K), the highest yield of acetaldehyde from dehydrogenation ethanol oxidation is produced by using Ag_xH_{3-x}PW₁₂O₄₀ catalyst^[6]. Zaki^[7], studied about the effect of transition metal from Fe₂O₃ and Mn₂O₃ in catalytic ethanol dehydration process. The result showed that there was an improvement in ethylene selectivity^[7].

Varisli et al^[8], also studied diethyl ether and ethylene production process with dehydration ethanol reaction on various catalysts. In this research, TPA (tungstophosphoricacid), STA (silicotungsticacid) and MPA (molydophosphoricacid) catalyst was used. The result showed that the highest Selectivity of ethylene (>0.75) was produced at 250°C with TPA catalyst. At temperature 180°C, the main product was diethyl ether. Furthermore, the presence of water vapor decreased the catalyst activity. Trends of Polyacid catalyst activity can be arranged from the largest value as STA>TPA>MPA^[8].

The recent research is objected to investigate the type of catalyst in ethanol dehydration process to produce diethyl ether. The types of catalyst, which are used in this research, are alumina, HZSM-5, and H-zeolit. In addition, H-zeolite is made of natural zeolite from Kabupaten Gunung Kidul district and Malang district.

II. MATERIALS AND METHODS

Zeolite is synthesized from natural zeolite, whereas chloride acid is produced from Brataco. AgNO₃ is used as indicator of chloride ion washing. Materials to create HZSM-5 catalyst are aquadest, waterglass, aluminium sulphate, sulphate acid, natrium hydroxide and amonium chloride. Materials for diethyl ether production process are tehcnical ethanol (95%) and nitrogen gas. ZSM-5 catalys is produced

based on Latourette, et al method ^[11]. Solution A which contains aluminium sulphate, sulphate acid and water is mixed with solution B which contains waterglass and aquadest. Solution C contains NaOH 40% which is added to solution A and B. Afterwards, this solution is stirred to make a homogenous solution at PH 9.5. After this step, the solution is placed and stirred in an autoclave with a heating at temperature 150°C within 24 hours. The produced crystal is washed, dried and calcinated. In order to get HZSM-5, the ion of the product is exchanged with ammonium chloride and continued with the washing, drying and calcinating.

In this experiment, alumina catalyst/aluminium oxide from a merck which have specification of surface area in the range of 190 m²/gram is used. As stated before, H-zeolite is produced from natural zeolite which is obtained from Wonosari district, Gunung Kidul district and Malang district. Characteristic of zeolite is shown in a result of the research of Widayat, et al ^[12]. The catalyst is produced with chemical treatment, washing, drying and calcination process. The chemical treatment is processed in three-neck flask which is equipped with cooler, water heater, and magnetic stirrer. Washing is processed to remove the Cl⁻ ion. Drying is processed with an oven at temperature 110°C. Calcination is processed with furnace which is equipped with temperature control. Catalyst product which is produced from natural zeolite of Gunung Kidul district is called KZ A, whereas the catalyst product from natural zeolite of Malang district is called KZ B. In addition, H-zeolite catalyst is synthesized by varying the ratio of the weight of zeolite and chloride acid solvent.

Catalytic test equipment is shown in figure 1. Fixed bed reactor is placed in a furnace. Feed/ethanol vaporizer tank and nitrogen gas is used as gas booster and inert. The condenser is used to condense the reaction product. The dimension of the fixed bed reactor is ½ inch of diameter and 1 gram of catalyst weight. In order to create catalyst bed, the reactor is equipped with mesh buffer and glasswool on the both side

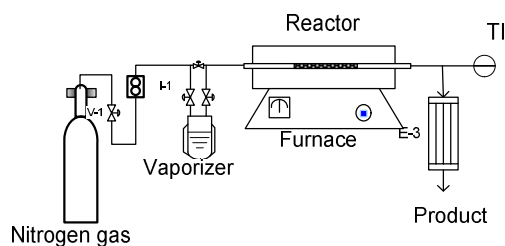


Figure 1. Ethanol dehydration process equipment

Diethyl ether production is processed with 1 gram of KZ A, KZ B, HZSM-5 and alumina catalyst at initial temperature 140°C, within 15 minutes. Ethanol vapor is boosted with nitrogen gas flow with a flow rate 200 ml/min. During 15 minutes, the product is condensed and analyzed with gas chromatography.

The characteristics is analyzed in instrumentation laboratory of Chemical Engineering Department FTI ITB. Crystalline characteristic with X ray Diffraction (XRD) is analyzed in Research Center ITS. The product is analyzed in chemical analysis laboratory Politeknik Negeri Malang by gas chromatography. The chromatography gas uses TCD detector

(Temperature Conductivity Detector) with helium gas as gas carrier with flow rate 20 ml/min, temperature 125- 250°C and detector temperature 275 °C. Components which are analyzed are diethyl ether, ethanol, water and methanol.

III. RESULTS AND DISCUSSION

Characteristics test is analyzed with X-ray Diffraction (XRD). Figure 2 shows the analysis result of the diffractogram analysis for zeolite catalyst with raw material from Gunung Kidul district (KZ A) and Malang District (KZ B). It can be observed that KZ A has more peak than KZ B at degree of theta 20-30. With a domination of Si composition, Catalyst tends to have a form as Silicate for KZ A and Modernite for KZ B. Intensity of KZ B catalyst is higher than KZ A catalyst. The difference of peak can also be observed at degree 2 theta 13 and 15, where the intensity of KZ A is higher than KZ B catalyst.

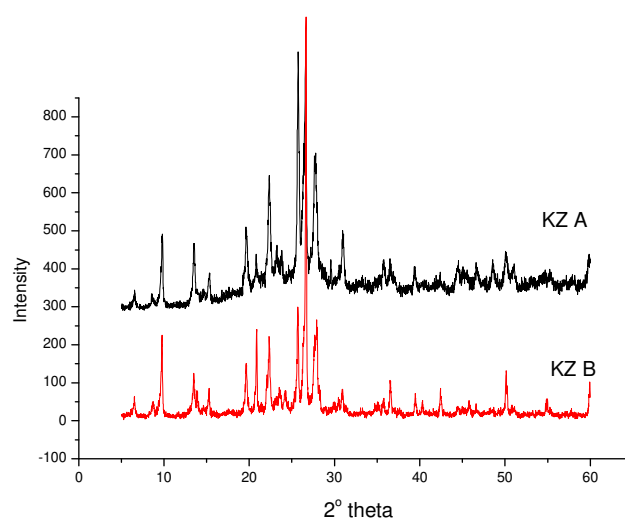


Figure 2. Diffractogram of H-Zeolite catalyst product

Crystallinity analysis result for variation of natural zeolite weight and solvent volume ratio is shown in figure 3. Figure 3 shows that all catalyst products have similar peaks. Most of each point in degree 2 theta have the similar peaks. This result is produced for both calcination or pre-calcination process. In addition, the peak height difference shows the difference of concentration.

XRD analysis result can be seen in figure 4. This figure shows standard and synthetic diffractogram HZSM-5 pattern. The specific peak of HZSM-5 is observed at a value of 2θ between 7-9° and between 22-25°. Based on the comparison between diffractogram pattern of synthetic and standard analysis, it can be concluded that both analyses give the same result. Therefore, it can also be concluded that the product of synthesis is HZSM-5. XRD analysis result from figure 3 has an amorphous form and shows an intensity at 2θ between 22-25°.

The next zeolite catalyst character analysis to investigate the surface area and total pores volume. Measurement of surface area and total pores volume using *Quantachrome NOVA 1000 High Speed Gas Sorption Analyser* dengan $P_0 = 711,65$ mmHg and nitrogen gas as adsorb gas/inert. Analysis result is shown in Table 1.

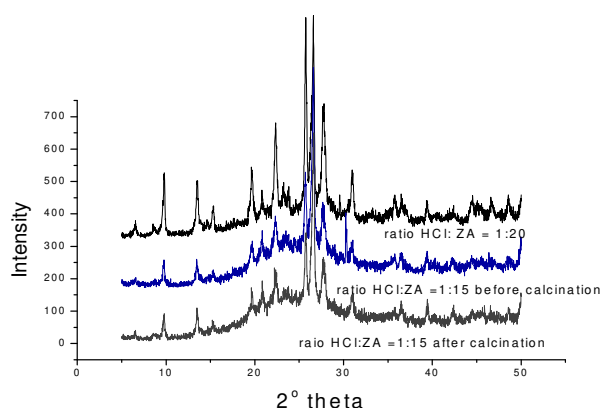


Figure 3. XRD diffractogram result of H-Zeolite catalyst: the effect of reactant ratio

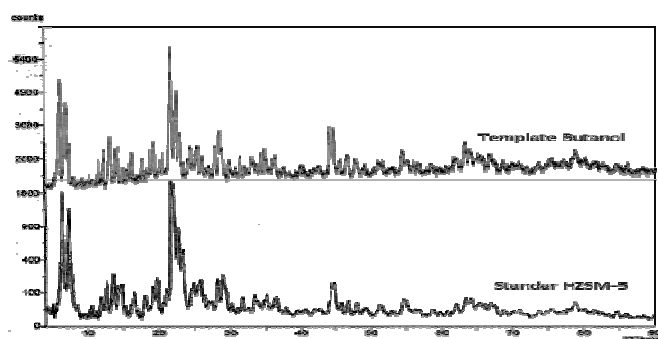


Figure 4. Analysis result of XRD HZSM-5 syntetic and HZSM-5 standart.

Table 1. Analysis results of surface area and total pore volume

Catalyst type	Specific surface area (m ² /g)	Pore volume (cc/g) x 10 ³
KZ A	184,5240	108,243
KZ B	130,2086	75,272
KZ A: 1/10	59,8937	35,511
KZ A: 1/15	135,7537	81,191
KZ A: 1/20	172,9295	101,763
KZ A: 1/30	70,4280	40,678
HZSM-5	149,918	-
Alumina	200	-

Table 1 shows that escalation of dealumination time have no significant effect to the surface area and total pores volume. In general, surface area of natural zeolite is around 20 m²/gram^[12]. Dealumination and calcination make some changes to the surface arean and total pores volume. Alumination causes escalation of Si/Al ration and aluminasi menyebabkan peningkatan perbandingan Si/Al dan dissolving of impurity CaO. The escalation ration of n SiO₂/Al₂O₃ causes a changes of zeolite structure. This changes is caused by Hydrolisis reaction and calcination process. The highest specific surface area and largest total pores volume are produced at dealumination time of 10 hours. Surface area of KZ B is smaller that KZ A catalyst product. In addition, table 1

also shows the escalation of surface area and total pores volume. The highest escalation id produced at ratio of Zeolite and HCl of 1:20.

Test result of Production process shows that the produced products contains methanol, water, diethyl ether and ethanol residue. This is shown in figure 5 and 6. Figure 5 shows chromatogram result for standart solution where water component is detected at retention time 3.38 min, methanol (RT 5.89 min), ethanol (RT 7.18 menit) and diethyl ether (RT 9.86 menit).

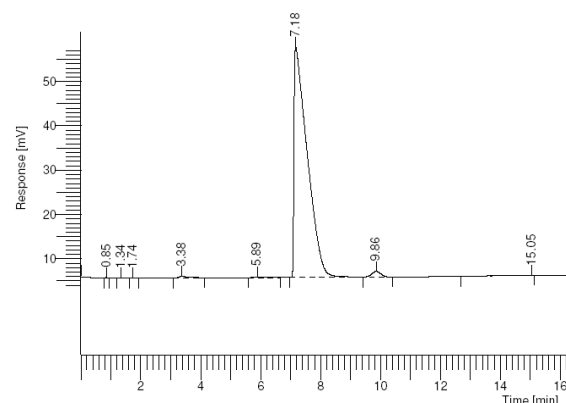


Figure 5. Chromatogram of standart solution

Chromatogram of dehydration process product is shown in figure 6. Figure 6a is chromatogram of diethyl ether production process result using alumina catalyst, whereas figure 6.b is using KZ A catalyst, figure 6.c using KZ B catalyst and 6.d using HZSM-5 catalyst. Alumina and H-zeolite catalyst (KZ A and KZ B) produces diethyl ether. Alumina catalyst is often used in ethanol dehydration process^{[2],[3]}. KZ A catalyst is silicalite, where its mainly component is silica that can be used as catalyst in diethyl ether production process. KZ B catalyst is zeolite with mordenite type that contains silica and aluminum that can be used for ethanol dehydration process. HZSM-5 catalyst does not produce diethyl ether, but produce a lot of water. From the reaction of ethanol conversion reaction, it can be analyzed that ethylene might be produced when HZSM-5 catalyst is used. Therefore, production process with HZSM-5 catalyst does not produce diethyl ether but produce ethylene. This is caused by the addition of water concentration in analysis result of gas chromatography (figure 6.d).

The next catalytic test of ethanol dehydration is data processing to calculate ethanol conversion and diethyl ether yield. The used of equation is as follow.

$$x = \frac{F_{A0} - F_A}{F_{A0}} \times 100 \% \quad (1)$$

$$\text{Yield of DEE} = \frac{\text{Mass of DEE (gram)}}{(F_{A0} - F_A) \text{ (gram)}} \times 100 \% \quad (2)$$

The result of calculation is shown in table 2. Table 2 shows that the largest ethanol conversion for natural zeolite from Gunung Kidul district is produced by KZ A 10 catalyst, whereas the largest ethanol conversion for natural zeolite from Malang district is produced by KZ B 15 catalyst.

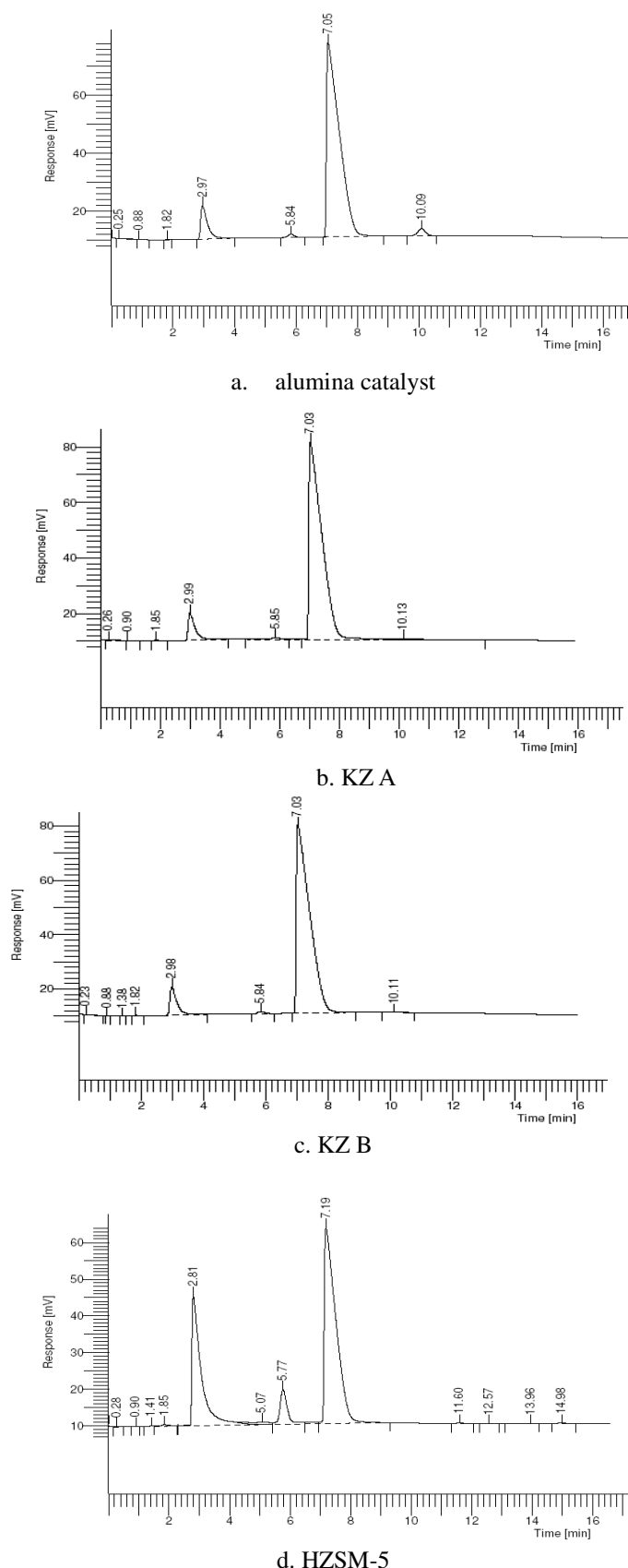


Figure 6. Khromatograph of liquid product ethanol dehydration

This is because KZ A catalyst has the largest surface area,

therefore the possibility of reaction is larger than the use of the other catalyst. In addition, Yield value of diethyl ether is smaller than dehydration process with alumina catalyst. Yield of KZ B is smaller than KZ A since the ration of Si/Al for KZ B > KZ A and surface area of KZ B is smaller than KZ A. Yield of diethyl ether for production process with HZSM-5 catalyst is 0 since there is no diethyl ether produced in the product.

Table 2 shows that the natural zeolite weight and chloride acid volume ratio affect to ethanol conversion. The higher reactant value the higher ethanol conversion. However, the conversion decrease after reactant ration of 1:20. The largest ethanol conversion is produced with ratio of zeolite weight and HCL volume is 1:20. This result follows the trend of catalyst surface area, but does not follow the trend of Si/Al ratio. This phenomenon shows that surface area and Si/Al ratio has an effect to ethanol dehydration process. Therefore, these two parameters need to be investigated into more detail.

Table 2. The result of ethanol conversion and DEE

Catalyst type	Ethanol conversion (%)	Yield DEE (%)
KZ A 10	4,68	1,78
KZ B 15	5,34	0,14
alumina	11,59	2,41
HZSM-5	56,44	0
KZ A: 1/10	15.27	2.98
KZ A: 1/15	34.66	0.21
KZ A: 1/20	39.28	0.85
KZ A: 1/30	6.78	1.35

IV. CONCLUSIONS

Result of this research can be concluded as follows; XRD analysis result of catalyst product showed that KZ A catalyst is H-zeolite with silicalite type and KZ B is H-zeolite with modernite type. The highest Specific surface area and total pore volume is 184,52 m²/gram and 108,243 x 10⁻³ cc/gram respectively at dealumination time 10 hours for KZ A catalyst. Production proess result of diethyl ether showed that alumina catalyst, KZ A and KZ B, can be used to produce diethyl ether. However, HZSM-5 could not be used to produce diethyl ether and only increase the amount of water and might produce ethylene. The largest yield of diethyl ether was produced alumina, KZ A and KZ B in decreasing order. The largest ethanol conversion of 56.44% was produced by using HZSM-5 catalyst. The higher value of natural zeolite and chloride acid solvent ratio the higher surface area and ethanol conversion. The highest ethanol was produced at reantant ration of 1:20.

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